Energy Exchange between Mesoparticles and Their Internal Degrees of Freedom

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Large-scale atomistic simulations enable a detailed understanding of complex, many-body problems in physics, chemistry, materials science, and biology. Unfortunately, despite the advances in methodologies and computer power, a wide range of phenomena is beyond present capabilities. In many of these cases, all-atom molecular-dynamics (MD) simulations are neither necessary nor desirable: coarse-grained descriptions of matter, where groups of atoms are described by a single mesoparticle, provide the required detail in a computationally efficient manner. The first task of mesodynamics is to describe the effective interactions between mesoparticles via a realistic mesopotential [1]. These mesoparticles can represent molecular groups in polymers, molecules in molecular crystals or grains in polycrystalline metals. While these approaches can be formulated to give accurate treatment of mechanical properties, there has been, up to now, no realistic thermomechanical treatment of the energy exchange between the mesoparticle and its internal degrees of freedom (DoFs).

The propagation of shockwaves in molecular crystals is particularly challenging to a mesodynamics description, since high energies and fast processes are involved. The shockwave initially excites long-wavelength, low-energy intermolecular DoFs (the ones described explicitly at the mesoscale), resulting in short-lived overheating of these (few) modes. Part of this energy then "cascades" to higher-energy, higher-frequency intramolecular DoFs, which are only implicitly treated in mesoscopic descriptions, on a time scale that depends on the details of the molecular vibrational spectrum. This equilibration process continues until the internal and molecular temperatures reach the same value. One hopes to formulate mesodynamics that accurately predicts the final shocked state of materials.

The local velocity $\langle \mathbf{u} \rangle_i$ in the neighborhood of a given particle i is defined in terms of its own velocity and the velocities of its neighbors $\mathbf{u}_j$, averaging over the neighborhood with a short-range weighting function $w(r_{ij})$ that decays monotonically with interparticle distance r_{ij}:

$$\langle \mathbf{u} \rangle_i = \frac{\sum_j w(r_{ij}) m_j \mathbf{u}_j}{\sum_j w(r_{ij}) m_j} \ , \qquad (1)$$

where the sum is over all particles. By analogy, the local neighborhood temperature T_i in d spatial dimensions is given by:

$$dkT_i = \frac{\sum_j w(r_{ij}) m_j \left| \mathbf{u}_j - \langle \mathbf{u} \rangle_i \right|^2}{\sum_j w(r_{ij})} \ . \qquad (2)$$

In the thermomechanical mesodynamics equations of motion, the local energy of the mesoparticle must be transferred from external to internal DoFs in a Galilean invariant manner. As consequence, the common practice of adding a viscous-damping deceleration term to the velocity update equation cannot be justified. We couple the local mesoparticle temperature T_i in the vicinity of particle i to the internal temperature T_i^0 by means of an additional contribution to the mesoparticle velocity in the coordinate update equation (rather than adding a viscous deceleration in the velocity update, as is customary in all other thermostatting techniques). The dissipative term contains a factor proportional to the temperature difference between internal and mesoscopic DoFs. The thermal energy of the internal DoFs is described via their specific heat C_i^0, which is in general a function of T_i^0. The mesodynamics equations of motion are then given by:

$$\dot{\mathbf{r}}_i = \mathbf{u}_i + \nu\left(\frac{T_i - T_i^0}{\theta}\right)\frac{\mathbf{F}_i}{m_i\langle\omega^2\rangle} \, ,$$

$$\dot{\mathbf{u}}_i = \frac{\mathbf{F}_i}{m_i} \, ,$$

$$\dot{T}_i^0 = \nu\left(\frac{T_i - T_i^0}{\theta}\right)\frac{\mathbf{F}_i}{C_i^0 m_i\langle\omega^2\rangle} \, , \qquad (3)$$

where ν is a coupling rate that determines the time-scale of equilibration between internal and external DoFs (it can be obtained by requiring the mesoscale description to match the equilibration rate of all-atom simulations).

As an example of this new mesodynamics with internal thermostats, we report here on shockwave propagation in the crystalline polymer poly (vinylidene fluoride) (PVDF), with monomer CH_2-CF_2 in its β phase (a polar crystal with all-trans bonds). The crystal is formed by infinite, parallel chains. In the plane perpendicular to the chains, it forms a quasihexagonal phase.

The all-atom MD simulations in this article were performed using an accurate force field denoted MSXX [2]. For the mesodynamics simulations, we represent each polymer chain by one mesoparticle in two dimensions (retaining the directions perpendicular to the polymer chains). The interaction between mesoparticles is a pairwise-additive Rydberg potential that reproduces the stress in uniaxial compression of PVDF as described by the MSXX potential.

Figure 1 shows the rise of the local temperature of a thin slab of material (one unit cell wide) as a shockwave with u_p = 3 km/s passes through it. In the all-atom MD simulations, we obtain two types of local temperatures: (1) the *molecular* temperature, defined as the fluctuations of the c.m. velocities of each polymer chain around the c.m. translational velocity of the whole slab; and (2) the *internal* temperature, defined as atomic velocity fluctuations around the c.m. velocity of each molecule. The two all-atom temperatures have well-defined counterparts in the mesoscopic description;
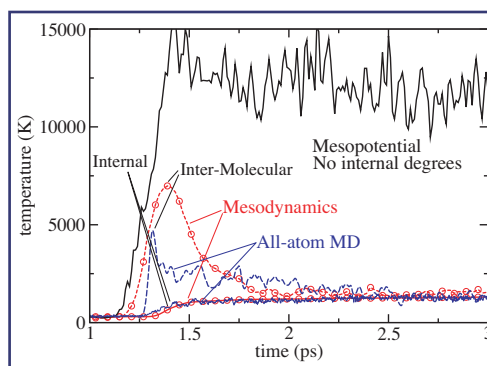

the internal temperature is just T_i^0, and the intermolecular temperature T_i is calculated from the velocity of the mesoparticles. The all-atom MD simulation (blue lines) shows that the shockwave initially excites the long-wavelength molecular modes; thus, the intermolecular temperature (dashed line) rises faster than the internal temperature (solid line) and initially overshoots its final value. As the higher-frequency internal DoFs get excited, intermolecular and intramolecular DoFs equilibrate, and both temperatures converge to the same value. The bare mesopotential without coupling greatly overestimates the final temperature, due to the reduced number of DoFs available to accommodate the energy increase. The new mesodynamics (red lines) correctly predicts the final temperature and rise times of the shocked material.

The new thermo-mechanical formulation of mesodynamics is generally applicable, extending the spatial and temporal range of more expensive all-atom simulations to thermodynamically realistic mesoscopic simulations, with the possibility of solving a wide variety of problems in physics, chemistry, materials science, and biology.

[1] B.L. Holian, *Europhys. Lett.* **64**, 330 (2003).
[2] N. Karasawa and W.A. Goddard III, *Macromolecules* **25**, 7168 (1992).

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Figure 1—
Time dependence of the local temperature of a thin slab of PVDF as a shock passes through. We show molecular and internal temperatures for all-atom MD, as well as mesodynamics, both with and without coupling to internal modes.

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